

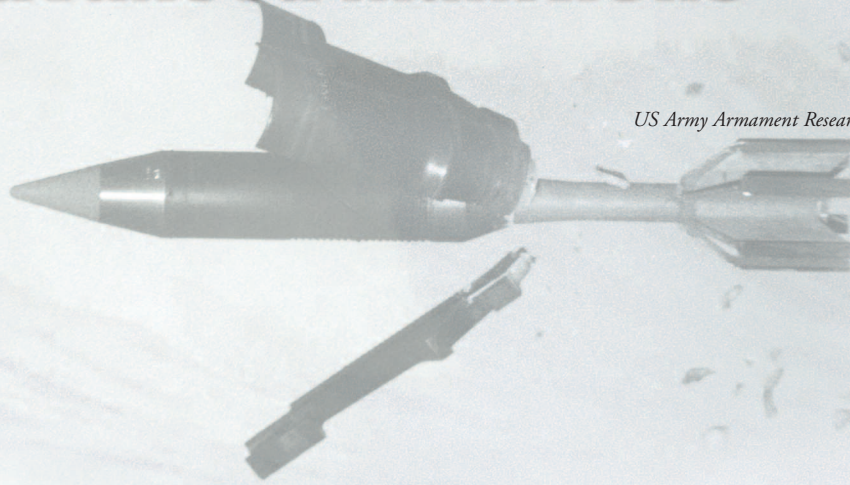
# An Overview of Novel Power Sources for Advanced Munitions

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## INTRODUCTION

Today's advanced gun-fired munitions, necessary for continuing operations and the Global War on Terrorism, require power sources with increased power and energy densities, all in a smaller package. Munitions power sources typically must operate over a wide temperature range (generally  $-45$  to  $145^{\circ}\text{F}$ ), withstand prolonged storage (10-20 years) prior to use, and survive the harsh environment of ballistic launch. Historically, thermal batteries have been used where high power was required for a relatively short time, and the munition rotated slowly, or not at all, as with rockets and missiles. Conversely, liquid electrolyte reserve batteries were better suited to the more moderately-powered, longer-lived electronic fuzes attached to rapidly rotating projectiles fired from the rifled barrels of large caliber artillery and some medium-caliber applications. This differentiation is due both to the capabilities of the electrochemical systems used in the respective application, and to the resulting differences in internal construction of the two battery types. Munition power sources are designed to be inert prior to deployment of the munition, which promotes long shelf life and enhances safety and reliability of the system. With the advent and continued proliferation of "smart" munitions, there is a need for power sources that have the best features of both thermals and liquid reserves: high power and high energy densities, with the ability to withstand high rates of spin. For some applications this may be realized with a hybrid approach, in which energy harvesters are used to supplement and/or substitute batteries as the munition power source. Regardless of their individual characteristics, the power sources should be as small as possible to maximize the lethality of the round, while also being safe, producible, reliable, and affordable.

US Army Armament Research Development & Engineering Center (ARDEC) has developed innovative power sources that offer a viable tactical solution for military applications and address the power lifecycle of smart munitions. Novel power sources for advanced munitions were developed at ARDEC under an Army Technology Objective (ATO) titled "Fuze and Power for

Advanced Munitions".\* This program addresses the development of power sources for artillery rounds, medium and small caliber munitions, missiles and rocket systems. The focus of ARDEC's efforts is to develop new energy sources, enhance the performance and capability of current power source components, and develop a systems approach to the management of power throughout the flight of munitions. This program was executed under the direction of ARDEC with the support from the Munitions Battery Team of the Army Research Laboratory (ARL) and a number of Small Business Innovative Research (SBIR) efforts.

The program execution is focused on developing technologies that define a munition's power system budget needs to address the mission profile for different munitions. To achieve this objective, the mission power profile has been identified as follows: (1) pre-launch power budget, (2) post-launch power budget and (3) flight power budget. The overall technical approach of this ATO program is to address those objectives that can be divided into three distinct areas:

- Improve thermal batteries by novel thermal management techniques that will result in longer lasting yet smaller batteries.
- Improve liquid reserve batteries with the development of catalyzed cathodes that provide higher power and energy densities plus new organic electrolytes that will lead to higher production throughput.
- Develop new types of energy harvesters to supplement and reduce the dependence on batteries (hybrid energy systems).

The program's mission is to develop advanced, affordable, onboard gun-fired munitions power sources technologies with increased energy and power densities, reduced volume and weight, increased mission time and improved extreme temperature performance. These technologies are broad-based and intended to be tailored for specific munition program applications. Successful incorporation of these technologies into existing and future programs is expected to increase lethality and enhance overall performance of smart munitions.

Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE <b>01 JAN 2009</b>		2. REPORT TYPE <b>N/A</b>		3. DATES COVERED <b>-</b>	
4. TITLE AND SUBTITLE <b>An Overview of Novel Power Sources for Advanced Munitions</b>				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) <b>Amabile, K Dratler, R McMullen, C</b>				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) <b>US Army Armament Research, Development and Engineering Center, Picatinny Arseanl, NJ</b>				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) <b>Defense Technical Information Center, Ft Belvoir, VA</b>				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT <b>Approved for public release, distribution unlimited</b>					
13. SUPPLEMENTARY NOTES <b>The original document contains color images.</b>					
14. ABSTRACT <b>Today's advanced gun-fired munitions, necessary for continuing operations and the Global War on Terrorism, require power sources with increased power and energy densities, all in a smaller package. Munitions power sources typically must operate over a wide temperature range (generally -45 to 145°F), withstand prolonged storage (10-20 years) prior to use, and survive the harsh environment of ballistic launch. Historically, thermal batteries have been used where high power was required for a relatively short time, and the munition rotated slowly, or not at all, as with rockets and missiles. Conversely, liquid electrolyte reserve batteries were better suited to the more moderately powered, longer-lived electronic fuzes attached to rapidly rotating projectiles fired from the rifled barrels of large caliber artillery and some medium-caliber applications.</b>					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT <b>UU</b>	18. NUMBER OF PAGES <b>10</b>	19a. NAME OF RESPONSIBLE PERSON
a. REPORT <b>unclassified</b>	b. ABSTRACT <b>unclassified</b>	c. THIS PAGE <b>unclassified</b>			

## RESEARCH EFFORTS

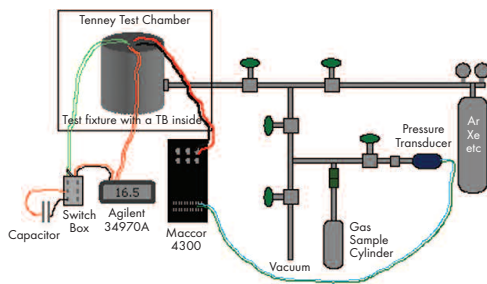
A significant portion of this four year program focused on investigating, developing and maturing various power source technologies. Specific areas of research in support of the thermal battery enhancements and liquid reserve battery improvements were led by ARL's Munitions Battery Team. The thermal battery efforts conducted under this program were focused on demonstrating the feasibility and benefits of introducing new heat management techniques into existing thermal batteries. The liquid reserve battery efforts were organized into two research areas: catalyzed cathodes and organic electrolytes. The purpose of the catalyzed cathode research was to investigate the effects of metal macro-cyclic complex catalysts on the current density of an existing battery. The focus of the organic electrolyte research was to develop a more benign electrochemistry that may be suitable for lower power munition applications. A team at ARDEC led the investigation and demonstration of the Hybrid Energy Systems (HES) technologies. The work conducted under this program was focused on developing and demonstrating new types of energy harvesters that would use the forces naturally resident in a gun-launched munition's environment and convert that into electrical energy, supplementing or reducing the dependence on electrochemical devices. The development of HES technologies was leveraged with the use of SBIR contracts. The leading HES component demonstrated under this program was the piezoelectric generator. This generator uses a spring mechanism to store the mechanical energy harvested from setback acceleration and flight vibration and then delivers the stored energy to a customized piezoelectric element. Prototypes were delivered and assembled into instrumented carriers which were integrated into a gun-launched munition and subjected to ballistic testing at Aberdeen Proving Ground (APG) and Yuma Proving Ground (YPG). The ballistic tests were used to validate performance and survivability of power source components in harsh operational environments. The remaining sections highlight the main research, development and integration efforts that were accomplished under this ATO program.

### Thermal Battery Novel Heat Management Techniques

Techniques to build thermal batteries with a longer lifetime or higher energy density are of paramount importance for the successful development and use of future smart munitions by the Army. The Low Cost Competent Munition (LCCM) thermal battery that had previously been developed at ARL was chosen as the benchmark. Efforts were focused on the effects and control of the internal operating gas atmosphere, optimal spatial distribution of heat source, and deployment of newer and better thermal insulation materials.[1] The investigation on the gas atmosphere was aimed at prolonging the lifetime of a thermal battery through



**Figure 1. LCCM thermal battery prototypes.**



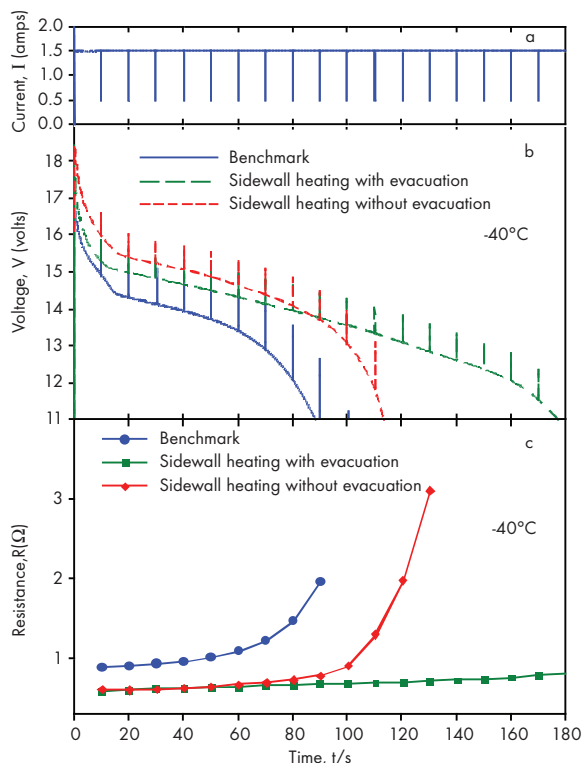
**Figure 2. A schematic of ARL's testing system for thermal batteries.**

the reduction of heat loss by eliminating the hydrogen component in the gas. This was carried out by evacuating a thermal battery during operation to demonstrate an extreme case of hydrogen elimination and by incorporating a gas getter in a battery for hydrogen reduction. The optimal spatial distribution of heat source materials was implemented by side- and end-wall heating with heat paper and heat pellets, respectively. The better thermal insulation was achieved by using thinner and more efficient thermal insulation materials in the battery.

The thermal battery components were made in a dry room from commercially purchased and in-house processed heat papers and cathode, anode, electrolyte, and pyrotechnic powders. The battery case of both the benchmark LCCM thermal battery and the improved versions measured 33.3 mm in diameter by 35.8 mm in height, exclusive of the external inertial igniter housing. The LCCM thermal batteries are shown in Figure 1. The thermal cell active stack was 19 mm in diameter with no center hole. For experimental work, ignition was accomplished by connecting a pre-charged capacitor with a piece of Nichrome wire buried in a heat paper pile, which in turn was connected with a heat paper fuse strip. For laboratory testing of the batteries, a heavy, sealable, and reusable steel test fixture was used to insure that the case temperature would remain near ambient temperature and closely approximate worst case heat sink conditions.[2] Figure 2 shows a schematic of the testing system for the thermal batteries. For this test, a Tenney Jr. Environmental Chamber was used to condition the test fixture at the test temperature of -40°C; a Maccor 4300 battery tester was used to apply the discharge load and record the voltage and pressure; an Agilent 34970A Data Acquisition/Switch Unit was used to monitor and record temperatures on the battery; a manual switch unit was used to initiate the battery and provide zero-time mark for other instruments, and a gas tubing manifold was used to monitor gas pressure, collect gas samples, and back-fill the battery with a selected gas when desired.

Prevention of rapid heat loss is a critical factor in prolonging operating lifetime as molten salt thermal batteries operate at temperatures as high as 600°C. For this reason, an operating gas atmosphere rich in a light element, such as hydrogen, is always to be avoided as has been demonstrated in our previous computational results.[3, 4] The experimental investigation of the effects of gas atmosphere in the lifetime of the LCCM battery was carried out by applying a vacuum of 7 Pa to a thermal battery during its operation and comparing the results with those of another battery without evacuation. The voltage profiles of the two, as shown in Figure 3b, demonstrate an increase in run-time for the evacuation condition (at cutoff voltage of 11 V) from 113 to 177 seconds, an improvement of almost 57%. Meanwhile, the internal resistance values, as plotted in Figure 3c, show that the application of evacuation had no effect on the internal resistances of the batteries. This



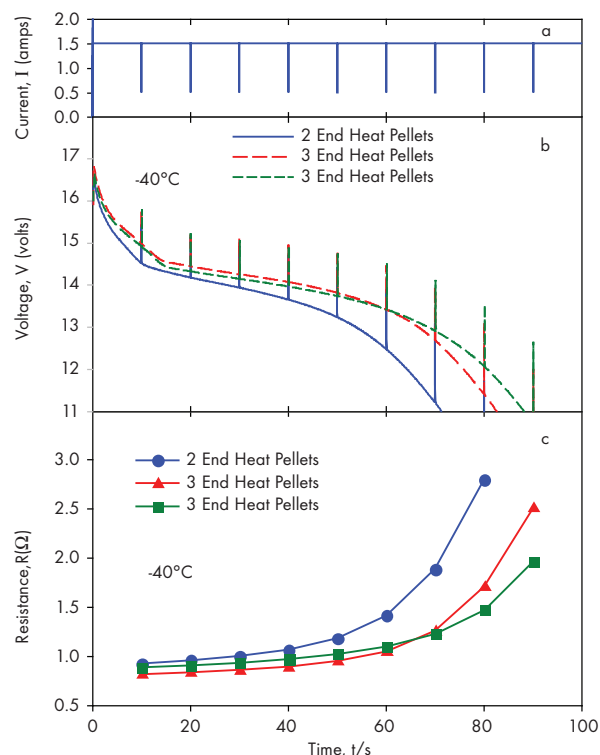


**Figure 3.** Voltage-time (b) and resistance-time (c) curves at a loading current (a) for different thermal batteries tested at -40°C.

is to be expected as the internal resistance measures the collective resistance to the passage of electrons and ions in the battery through only solid phases. These internal resistance values were calculated from the curves in Figures 3a and 3b by the equation  $R = \Delta V / \Delta I$ , where  $\Delta I$  is the drop of current in a current pulse shown in 3a, which in this case is 1 A, and  $\Delta V$  is the corresponding jump in a voltage curve in 3b.

It is imperative that a sufficient amount of heat be provided in a thermal battery for proper operation. It is equally important that this heat source be spatially distributed in such a way that the heat generated can efficiently create a sustained uniform high temperature zone in the battery stack without local temperature spikes. In this sense, the traditional way of having pyrotechnic heat pellets stacked and interlaced with the thermal cells as the only source of heat supply is far from ideal. On one hand, it runs the risk of overheating the thermal cells while on the other hand it sets up very high temperature gradients both radially and axially causing rapid heat losses. One of the most effective and direct ways of remedying the situation is to add extra heat to the thermal insulation in the battery stack ends. Extra heat may also be placed in the insulation sidewall. This was attempted using different numbers of end heat pellets in benchmark thermal batteries to observe the effects and to obtain an optimal number of heat pellets.

Figure 4 shows the results of voltage profiles and resistance values for different numbers of end heat pellets. As shown in Figure 4b, the run-time of the batteries increases steadily with the increase in the number of heat pellets, up to four. The resistances change accordingly as shown in Figure 4c. A higher number of end heat pellets not only provides more heat for bringing the battery internals above the eutectic point of the electrolyte but

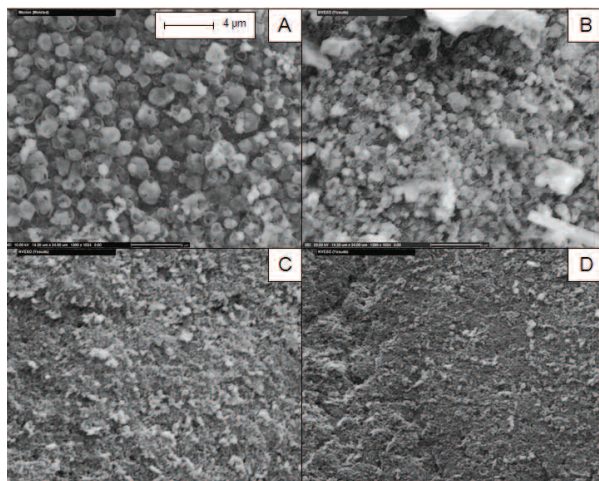


**Figure 4.** Voltage-time (b) and resistance-time (c) curves at a loading current (a) for thermal batteries with varying numbers of end heat pellets.

also prevents rapid heat loss from the end thermal cells. The case of side-wall heating is demonstrated in Figure 3, between the curves of the benchmark battery and those of the battery without evacuation but with its side-wall heated by a layer of heat paper and with Microtherm as the thermal insulation material. The combined effects of side-wall heating and improved thermal insulation resulted in an increase in the lifetime of the battery from 88 to 113 seconds, an improvement of 28%, shown in Figure 3. Although it cannot be determined from the experiments so far just how much of the 28% is due to the side-wall heating alone, it is believed to be significant. For this purpose of heating the side-wall, research efforts have also focused on the investigation and experimentation with nano-layered bimetallic foils as the alternative materials, and found them to be very promising due to a unique and special set of properties. [5, 6]

#### High Rate and High Energy Oxyhalide Battery

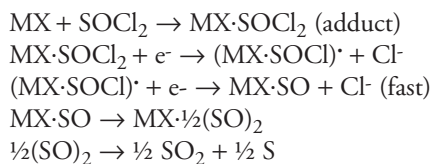
In the last two decades, lithium-based batteries have become the predominant energy system for the electronic fuzes used in large caliber artillery applications. These batteries typically use lithium metal as the anode, thionyl chloride ( $\text{SOCl}_2$ ) or sulfuryl chloride ( $\text{SO}_2\text{Cl}_2$ ) as the electrolyte/liquid cathode (catholyte), and porous teflonated<sup>†</sup> carbon pads as the reaction site. For the sake of simplicity, these Teflonated carbon pads will be referred to as “cathodes” here because, at least structurally, they serve as the positive electrode in this system. The object of the research effort under this program was to significantly increase the power and energy capabilities of the current Multi-Option Fuze for Artillery (MOFA) battery simply by adding catalyst(s) to the cathode. The MOFA battery uses  $\text{SOCl}_2$  as the catholyte, and was



**Figure 5.** SEM images of porous MOFA carbon cathodes, (A) containing 4.7% (w/w) total Co-SB and Co-TMPP, discharged at 75 mA/cm<sup>2</sup>; (B) cathode without catalyst, discharged at 75 mA/cm<sup>2</sup>; (C) 4.7% total catalyst, prior to discharge; and (D) cathode without catalyst, prior to discharge. All images are the same scale indicated in (A).

designed to operate at a current density of 35 mA/cm<sup>2</sup>. Because of previously-demonstrated expertise in this area, PowerCell Technologies was tasked with this research and development effort, which was conducted primarily at ARL facilities.

At low-rate discharges (<5 mA/cm<sup>2</sup>), the electrochemical reduction of SOCl<sub>2</sub> on porous teflonated carbon cathodes is not diffusion-limited, and the use of catalysts does not improve capacity. However, at higher rate discharges, the primary cause of cell failure in cathode-limited Li/SOCl<sub>2</sub> cells is the formation of a lithium chloride (LiCl) passivation film on the surface of the carbon cathode that creates a diffusion limitation. The use of metal macrocyclic complex catalysts, including metal phthalocyanines, metal phenylporphyrins, and metal quadridentate Schiff bases (MX), is believed to increase capacity due to the courser grain structure of the LiCl film, allowing extra porosity for continued penetration of SOCl<sub>2</sub> into the carbon cathode. Changes to the cathode surface, both before and following cell discharge, can be seen in Figure 5. These electrocatalysts also alter the mechanism of electrochemical reduction of SOCl<sub>2</sub>, resulting in higher rate capabilities over non-catalyzed systems:

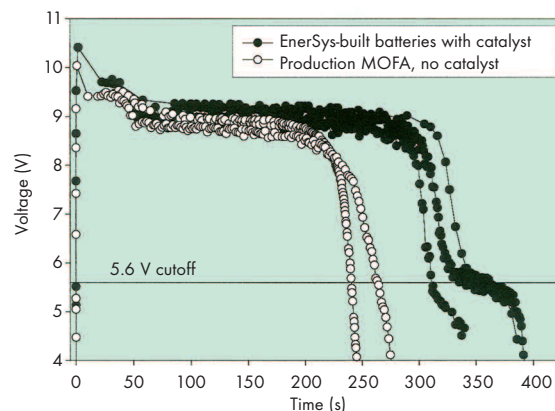


A combination of cobalt Schiff base (Co-SB) and cobalt tetramethoxyphenylporphyrin (Co-TMPP) was used as the catalyst in this study. Based on the results of lab cell testing, it was believed a current density of 75 mA/cm<sup>2</sup> could be achieved by adding the catalysts to the production cathode material, and incorporating this material into an otherwise unaltered production battery. Cathode material used in manufacturing the MOFA battery was obtained from EnerSys Advanced Systems, the battery's producer. The catalysts were impregnated into the base cathode material by dissolving them in an appropriate solvent, and then dipping the cathode material into the resulting solution.

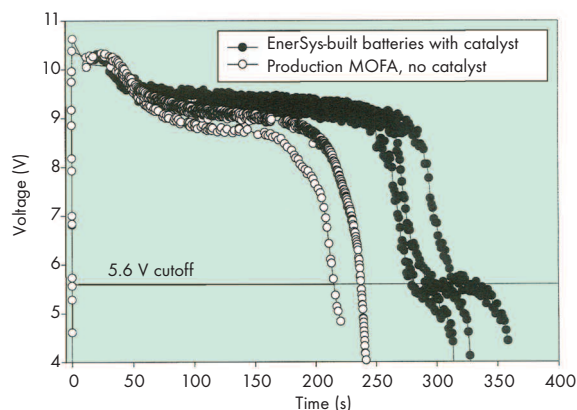


**Figure 6.** Enhanced liquid reserve MOFA battery prototypes.

Prototype batteries were built at ARL, as shown in Figure 6, which use this material and then were tested against standard production batteries, which served as the controls. Significant increases in discharge life were observed throughout the typical operating temperature range of -45°F to 145°F. Finally, a length of cathode material was impregnated with catalysts at ARL and



**Figure 7.** Discharge performance of EnerSys-built batteries, with and without catalysts, at 75 mA/cm<sup>2</sup> and 70°F.



**Figure 8.** Discharge performance of EnerSys-built batteries, with and without catalysts, at 75 mA/cm<sup>2</sup> and 145°F.

then provided to EnerSys, where it was built into special engineering units using the MOFA battery production equipment. Because of some processing issues at ARL, this material only contained about half as much catalyst as intended, but the engineering batteries still performed significantly better than the controls at 70°F (Figure 7) and 145°F (Figure 8), and about the same at -45°F (Figure 9). However, earlier results (Figure 10) indicated that improved performance should also be possible at the low temperature extreme.

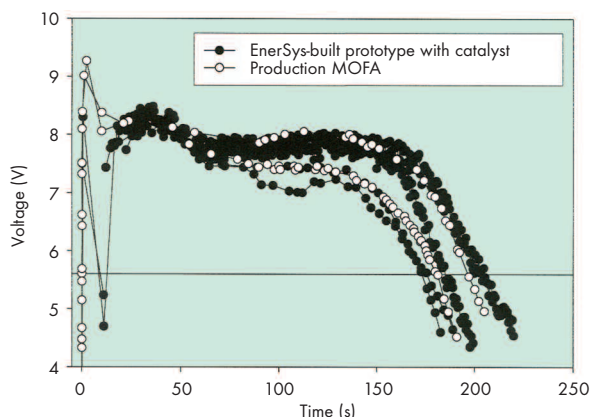
### Organic Electrolyte-Based Lithium Reserve Batteries

While  $\text{Li}/\text{SOCl}_2$  and  $\text{Li}/\text{SO}_2\text{Cl}_2$  batteries have proven themselves to be very capable, this electrochemical system can create significant design and manufacturing issues, as the catholytes are extremely hygroscopic and turn highly corrosive when exposed to moisture. Only a very few materials can withstand prolonged exposure even in the absence of moisture. Thus, material selection is limited and critical during the design phase. And since even the best dry rooms are not completely moisture-free, the manufacturing equipment that fills and seals the catholyte container is constantly being degraded by exposure and generally requires frequent maintenance. Finally, the combination of high vapor pressure and high ionic salt content typically found in catholyte formulations has caused fouling issues with dispensing equipment, particularly in the attempted manufacture of very small reserve batteries intended for use in submunitions and medium caliber applications. As a result, a research effort was launched to develop a more benign electro-

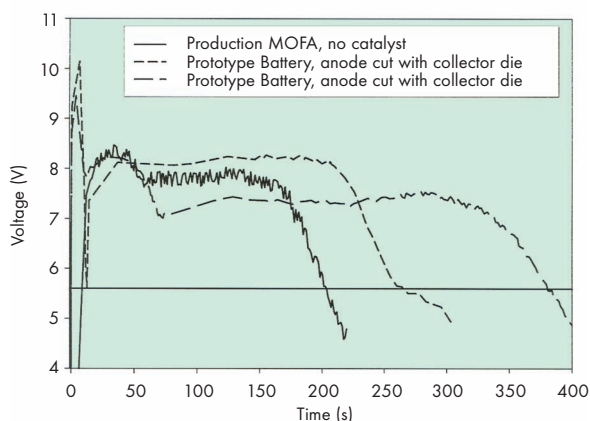
chemistry that also showed the potential for acceptable discharge performance over the typical Army operating temperature range of -45 to 145°F. The power requirement for this program was a relatively low current capability, about 5 mA/cm<sup>2</sup> at 3 volts, which were established as performance goals.

MaxPower, Inc. was awarded a contract to select or develop an appropriate electrochemical system, demonstrate suitable performance, and conduct preliminary storage stability studies. Following an initial down-selection process based on existing literature and company experience, and focused experimentation performed under this program, MaxPower selected to investigate an electrochemical system that used lithium metal as the anode, the  $\lambda$ -form of  $\text{MnO}_2$  as the cathode, and one molar LiBETI/EA (bis(perfluoroethanesulfonimide) in ethylene acetate) as the electrolyte. This electrochemical system has its basis in lithium-ion secondary battery technology, with a significant amount of existing data for some of the individual components. The selected electrochemistry has a working voltage of approximately

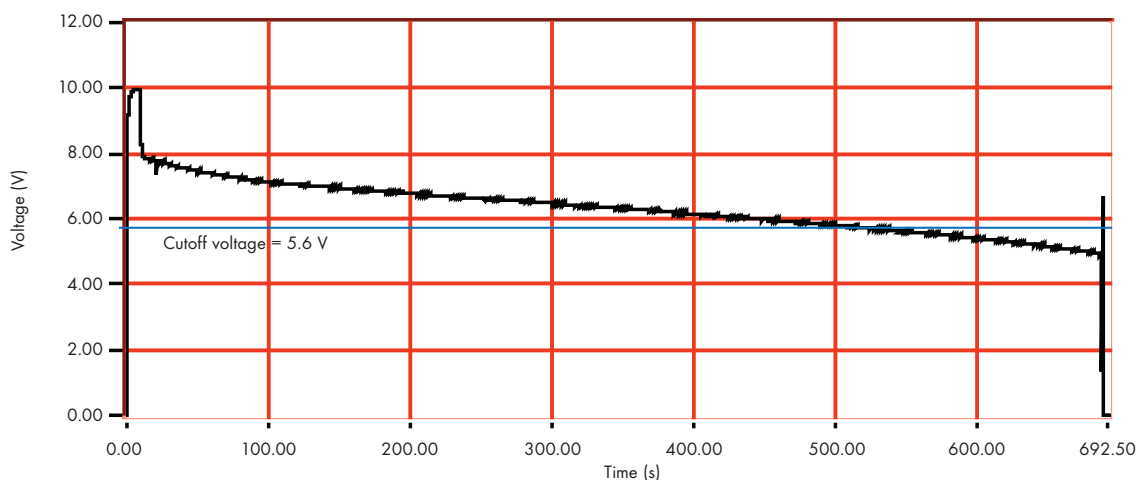
2.4-2.7 volts at the 5 mA/cm<sup>2</sup> rate, but since the batteries that would be built for demonstration would be of a series-cell design, that was acceptable. In fact, as with the catalyzed-cathode project, the MOFA application was used as a yardstick for the organic-electrolyte system due to the availability of production battery components and a highly-developed testing procedure. Discharge performance of the selected organic electrolyte system versus the MOFA requirement (pro-rated) is shown in Figure 11.



**Figure 9. Discharge performance of EnerSys-built batteries, with and without catalysts, at 75 mA/cm<sup>2</sup> and -45°F.**

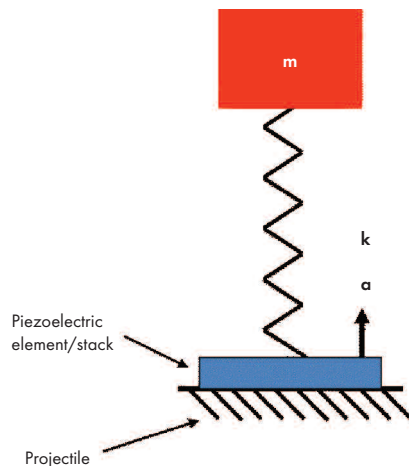


**Figure 10. Discharge performance of batteries, discharged at 75 mA/cm<sup>2</sup> and -45°F.**



**Figure 11. Discharge performance of the organic-electrolyte system at 4.5 mA/cm<sup>2</sup> and 70°F.**





**Figure 12. Piezoelectric basic concept.**

The battery activates under a light (1000 ohms) load, and then at ten seconds into the discharge, a load equating to a 4.5 mA/cm<sup>2</sup> current density is switched in for the remainder of the discharge. In reality, a medium- to high-rate battery like MOFA would not be an ideal application for the organic-electrolyte system because of the organic system's significantly lower rate capability. However, low-rate applications do exist, and it is believed that the more-benign chemistry of the organic system will make it desirable in those situations.

To date, there have been limited efforts conducted to demonstrate long (10-20 year) shelf life for the organic system as a complete package. However, during down-selection of the electrochemical cell components, primarily the cathode, a significant amount of existing data and theory was reviewed to initially select candidate materials. The candidates were then subjected to variations in formulation, processing, and evaluation in an effort to gain further insight into their stability. Materials that showed the greatest promise were stored at elevated temperatures for up to six months, and then tested in laboratory cells against fresh materials. Those samples that showed any significant degradation in performance were dropped from consideration. Some of the candidate materials have been used in rechargeable battery applications, so there is some history with them. How well they apply to the uniqueness of the reserve battery application remains to be investigated.

### Hybrid Energy Systems – Piezoelectric Energy Harvesters

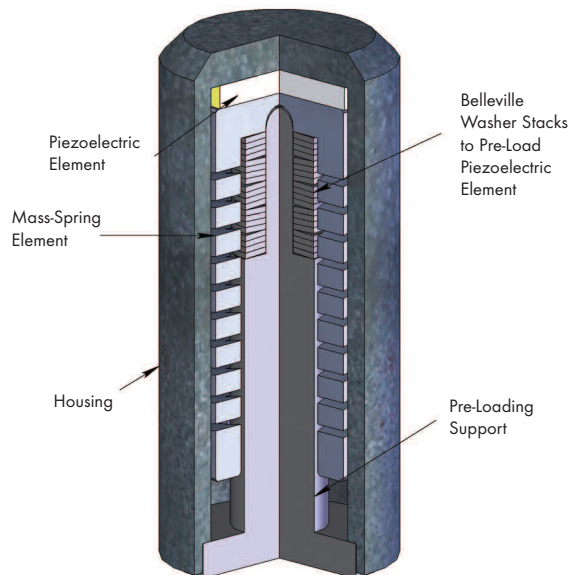
The continuous stacked piezoelectric energy harvester as shown in Figure 12, consists of a mass and spring configuration designed to be in resonance at a frequency of oscillation  $f_o = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$ . [7] The mass,  $m$ , is attached to a moving platform by a spring. The frequency of oscillation is controlled by the spring constant,  $k$ , and the value of the mass. If the moving platform is accelerated upward by an acceleration,  $a$ , as encountered during setback acceleration during gun launch, then the spring will compress a distance,  $d$ , required to balance the force generated by the accelerating mass. As a result, a potential energy  $PE = (\frac{1}{2}) k d^2$  is stored in the compressed spring.

Once the projectile exits the gun barrel, the mass-spring system begins to vibrate, generating a recurring load on the piezoelectric element. The stored potential energy PE can then be harvested by

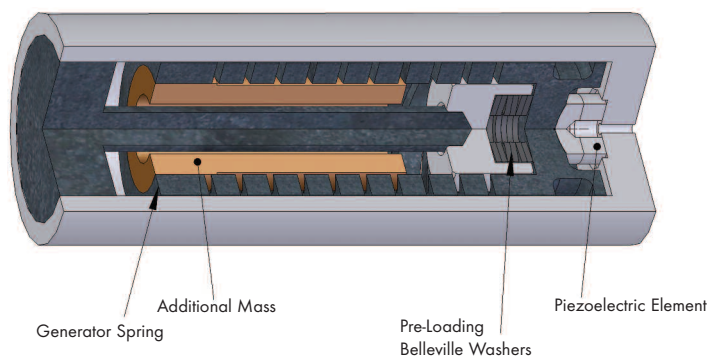
extracting the charge generated on the piezoelectric element by the recurring load. During the flight, movement of the projectile due to forces resulting from ballistic environment would also result in the vibration of the mass spring system and mechanical energy could be harvested by the piezoelectric element. The test results have shown that efficiencies up to 33% in converting the available mechanical energy to electrical energy (including the power collection and regulation electronics) can be achieved.

The energy resulting from vibration is stored on the mass-spring combination and delivered to the stacked piezoelectric crystal as the mechanical system reaches resonance. An important component of this system is the Belleville washer that preloads the stacked piezoelectric crystal to prevent breakage under stress. The Belleville washer will ensure there is always a compressive force on the piezoelectric crystal. Without the washer, the harsh environments typically encountered during gun launch and flight may damage the piezoelectric energy harvester.

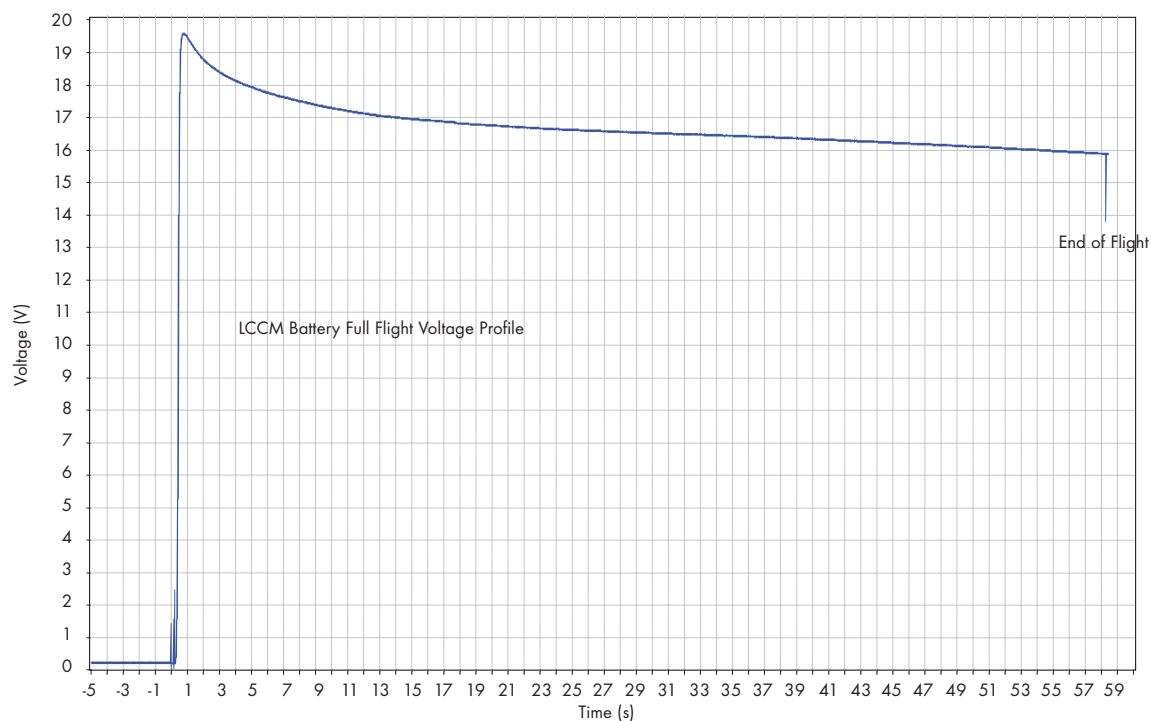
The methods used to harvest electrical energy for the axial design, as shown in Figure 13, are very similar to the radial design, as shown in Figure 14. The main difference is that each device would be tuned to the acceleration profile expected during the flight of the projectile (axial acceleration vs. radial acceleration). Another important distinction of this novel continuous piezoelectric energy harvester application is the use of a stacked



**Figure 13. Axial piezoelectric energy harvester.**



**Figure 14. Radial piezoelectric harvester.**



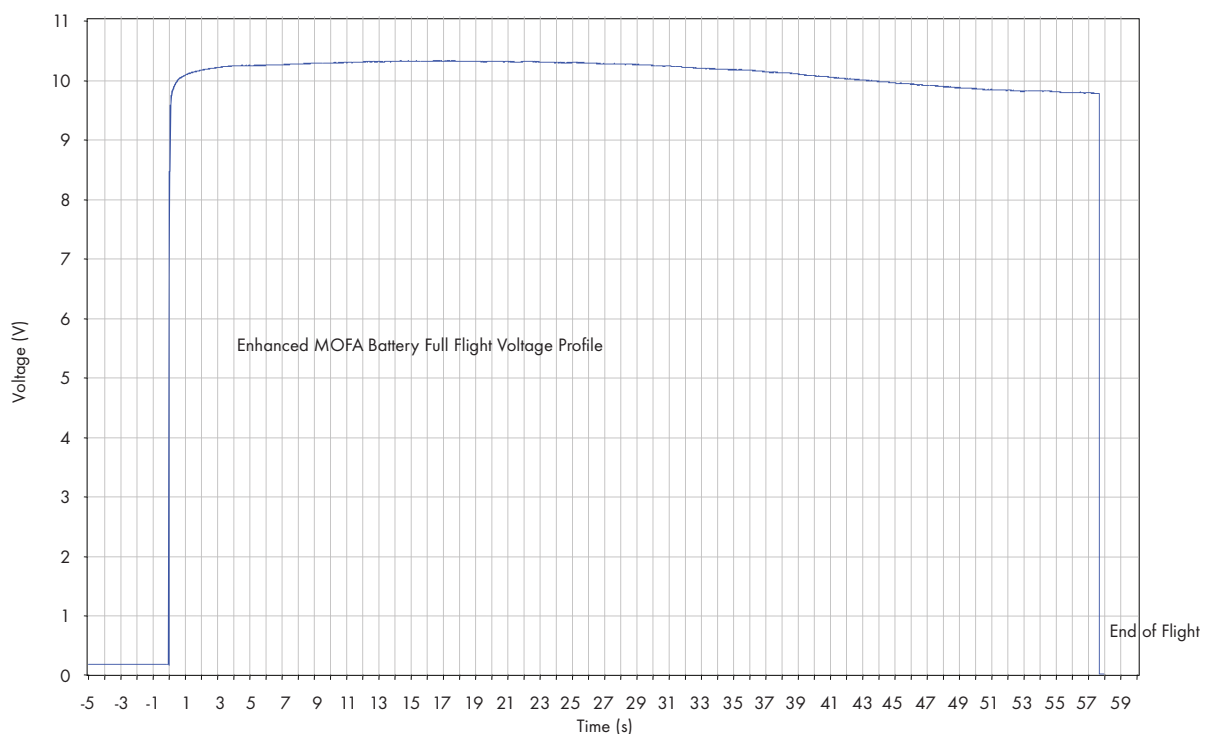
**Figure 15. Results of flight testing improved LCCM thermal battery prototype at YPG (10 ohm load).**

piezoelectric material that is comprised of multiples layers. Typically in piezoelectric applications, others have attempted to use single layer piezoelectric crystal devices to harvest energy. However, single layer devices will provide a response to mechanical vibration that is larger in amplitude but narrower in duration. This is not a implementation as a higher voltage in a shorter time is more difficult to regulate and not as efficient in harvesting energy of the pulse. For this reason stacked piezoelectric crystals will

perform superior to a single piezoelectric layer by providing smaller amplitudes of voltage and lasting for much longer periods of time.

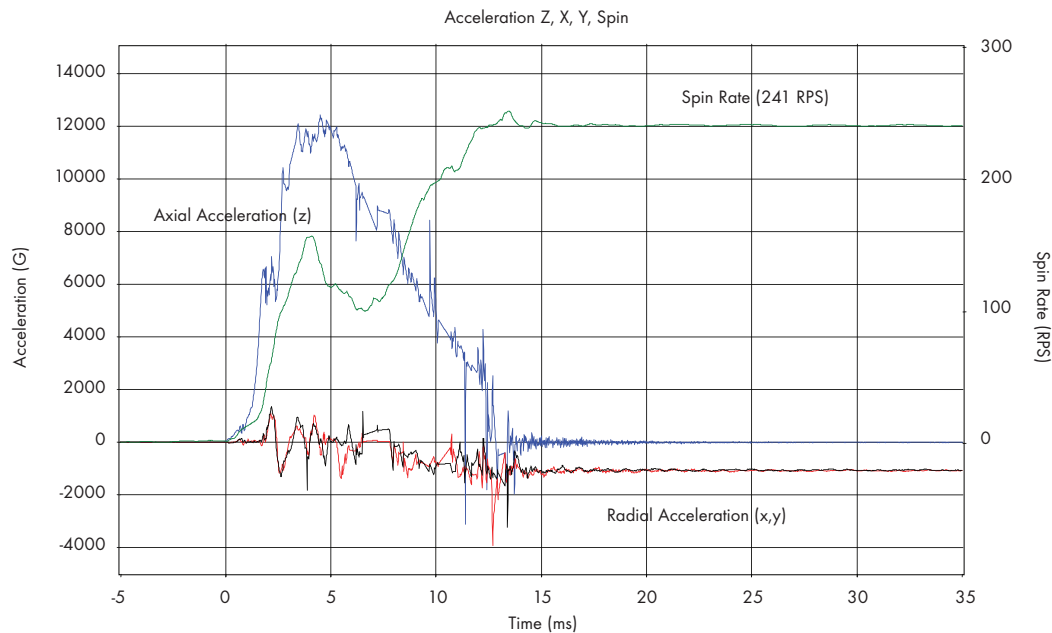
#### BALLISTIC TEST RESULTS

Flight tests consisted of packaging the power sources into gun-launched munitions for nominal tactical demonstrations. The power source prototypes were monitored with a telemetry system



**Figure 16. Results of flight testing-enhanced catalyzed liquid reserve MOFA battery prototype at YPG (12.66 ohm load).**





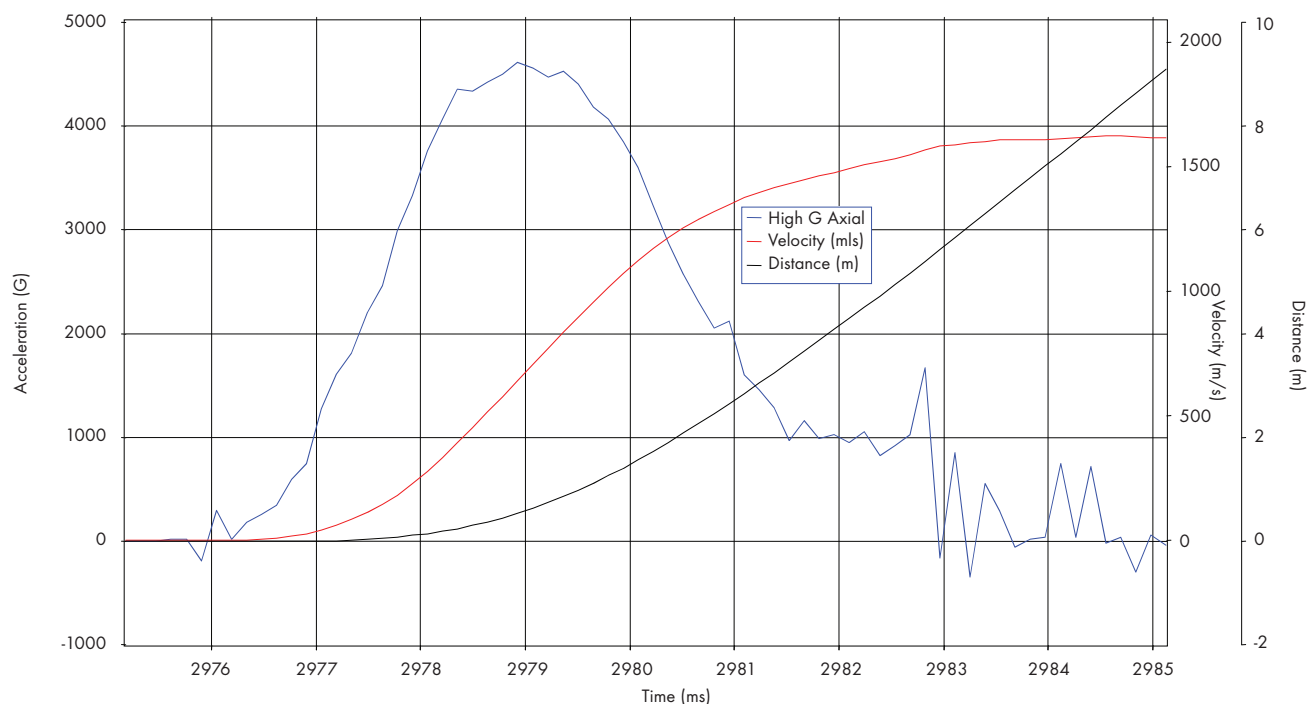
**Figure 17. Typical acceleration and spin profile of M549 projectile.**

via 'telemetry carriers', which allowed monitoring of component performance during testing, and the ability to record the data for analysis. The flight test validated a Technical Readiness Level (TRL) 7 (at a component level) for each component that demonstrated a successful test.

Prototypes of the enhanced thermal batteries, improved liquid reserve batteries (catalyzed cathodes) and hybrid energy systems (piezoelectric generators), were delivered, integrated on the M830A1 tank round and the M549 artillery round. They were then tested at APG or YPG, with results shown in Figures 15 and 16.

As shown, the improved LCCM thermal battery prototypes

operated significantly longer than the benchmark batteries, consistent with the laboratory results achieving 30% increase in run-time and 30% increase in energy density. The enhanced MOFA liquid reserve catalyzed battery prototypes discharged at slightly higher voltages with an increased power density and increased run-time. The performance of the improved thermal and liquid reserve battery prototypes surpassed the program exit criteria. These prototypes survived the launch conditions with regard to acceleration (12,000-14,000 G) and high spin rate (average 240RPS), as shown in Figure 17, thereby successfully reaching TRL level 7.



**Figure 18. Typical acceleration plot of M830A1 tank round.**

The piezoelectric generators produced 23 mW of electrical power harvested from axial and radial acceleration which successfully achieved the program requirement of 20 mW of power. The future design of piezoelectric energy harvesters can be optimized enabling additional energy to be harvested by matching the resonant frequency of the mass spring system to that of the munition. Additionally, the piezoelectric generators survived the high acceleration forces (45,000 G) encountered during gun-launch. Typical acceleration plots of the setback environment can be found in Figure 18.

## SUMMARY

The technologies evaluated and integrated under this program achieved the overall program objectives of increased performance, energy density and increased power density, improved temperature performance, as well as the development of new energy harvesting devices that use the ballistic environment to generate electrical energy. The robust packaging and configurations of the thermal battery improvements, liquid reserve battery enhancements and energy harvesters have withstood the harsh environments encountered during gun launch on tank rounds and artillery rounds. These technologies are broad based and intended for use in any gun launched munition by tailoring the configurations to meet specific program requirements. Additionally, the investigation and laboratory demonstration of the organic electrolyte shows that the chemistry is less corrosive than the typical oxyhalide chemistries that are typically used. This represents a viable alternative to the more common oxyhalide chemistries for less demanding power applications. The technologies developed from this program will produce a positive impact to the warfighter, enabling safe, affordable, reliable and decisive military superiority. The test results validate that these technologies will help the warfighter safely meet their operational objectives by greatly enhancing lethality.

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## ACKNOWLEDGEMENTS

This project was made possible by the collaboration and teamwork between US Army ARDEC and ARL; the contractual relationships between ARL and PowerCell Technologies, ARL and MaxPower, Inc., as well as US Army ARDEC and Omnitek Partners, LLC.

A special acknowledgement goes to Dr. Michael Ding and Mr. Jeff Swank of ARL for their contributions to this article as well as Mr. Richard Dratler and Mr. Chuck McMullan for their contributions to the Power Sources ATO Closeout Report.[7]

The authors gratefully acknowledge the support of US Army ARDEC's Telemetry Team led by Mr. Boris Flyash, Mr. Mauricio Guevara and Mr. Lam Vo; and senior advisors Mr. Chris Janow and Ms. Maria Allende of US Army ARDEC.

## NOTES & REFERENCES

\* D.LE.2006.01

† Teflonation is a process involving mixing aqueous colloidal Teflon® emulsion with a powdered material, adding methanol to coagulate the Teflon®, followed by cleaning and drying. Teflon® is a registered trademark of E. I. du Pont de Nemours and Company Corporation.

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